Temperature dependence of factors controlling isoprene emissions

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[1] We investigated the relationship of variability in the formaldehyde (HCHO) columns measured by the Aura Ozone Monitoring Instrument (OMI) to isoprene emissions in the southeastern United States for 2005–2007. The data show that the inferred, regional-average isoprene emissions varied by about 22% during summer and are well correlated with temperature, which is known to influence emissions. Part of the correlation with temperature is likely associated with other causal factors that are temperature-dependent. We show that the variations in HCHO are convolved with the temperature dependence of surface ozone, which influences isoprene emissions, and the dependence of the HCHO column to mixed layer height as OMI's sensitivity to HCHO increases with altitude. Furthermore, we show that while there is an association of drought with the variation in HCHO, drought in the southeastern U.S. is convolved with temperature. **Citation:** Duncan, B. N., Y. Yoshida, M. R. Damon, A. R. Douglass, and J. C. Witte (2009), Temperature dependence of factors controlling isoprene emissions, *Geophys. Res. Lett.*, *36*, L05813, doi:10.1029/2008GL037090.

1. Introduction

[2] Atmospheric formaldehyde (HCHO) is a ubiquitous volatile organic compound (VOC) that is a secondary product of the oxidation of methane and many other VOCs. In the southeastern United States, mixed layer concentrations of HCHO are particularly high in summer. The dominant source of this HCHO is the oxidation of biogenic isoprene that is emitted from some trees and plants [*Palmer et al.*, 2003, 2006]. In Houston, the oxidation of anthropogenic VOCs is another important source [*Martin et al.*, 2004]. Variations in observed HCHO columns serve as a proxy for variations in isoprene emissions in most of the southeastern U.S. [*Palmer et al.*, 2003, 2006; *Millet et al.*, 2008]. In this region, isoprene plays an important role in the formation of photochemical smog [*Chameides et al.*, 1988].

[3] Thermotolerance is the likely reason why some plants emit isoprene, though isoprene appears to also provide protection from oxidants such as ozone [*Sharkey et al.*, 2007, and references therein]. A number of factors cause isoprene emissions to vary in a given plant, including light intensity, leaf age, and several meteorological variables [*Guenther et al.*, 2006]. Laboratory experiments [e.g., *Tingey et al.*, 1979] and inferred emissions from the space-borne Global Ozone Monitoring Experiment (GOME) instrument [e.g., *Abbot et al.*, 2003] show that isoprene emissions are a strong function of temperature.

[4] Another factor that may contribute to the variability of isoprene emissions is the complex response of various plant species to drought. In general, studies of the response of plants to cycles of drying and rewatering have found that while photosynthesis is severely inhibited by short-term drought (i.e., up to the point of plant wilting), the emissions of isoprene are only modestly inhibited and often recover or exceed pre-stress rates after rewatering [e.g., *Fang et al.*, 1996; *Pegoraro et al.*, 2004; *Brilli et al.*, 2007, and references therein]. These studies generally concluded that the relative insensitivity of isoprene emissions to short-term drought, as compared to the strong sensitivity of photosynthesis, suggests the importance of isoprene in protecting plants from environmental stresses. Both photosynthesis and emission of isoprene effectively stop during long-term drought [e.g., *Pegoraro et al.*, 2004], especially for saplings and other plants and trees with shallow roots that do not tap the water table.

[5] Here we examine the credibility and causes of variability of isoprene emissions in the southeastern U.S. for 2005–2007 as inferred from HCHO data from the Ozone Monitoring Instrument (OMI) on the Aura satellite [*Levelt et al.*, 2006]. We show that the temperature dependence of the inferred isoprene emissions is likely convolved with other temperature-dependent factors (e.g., drought) that also act to enhance emissions with increasing temperature.

2. OMI HCHO Observations

[6] The Aura OMI is a nadir-viewing UV/Vis solar backscatter instrument; the specifics of the HCHO algorithm are described by *Chance* [2002] and *Kurosu et al.* [2004]. The satellite was launched in July 2004 and crosses the equator at 1338 local time in the ascending node, close to when isoprene emissions are near their daily maximum. HCHO fitting was performed in the spectral window 327.5–356.5 nm. We use the level-2 gridded product (v003), which is a vertical column with a horizontal resolution of 0.25° latitude by 0.25° longitude. We regridded the product to 1° latitude by 1.25° longitude, so as to match the grid of the GEOS-5 assimilated meteorological fields [*Rienecker*, 2007] that we use in this study. We then created monthly averages, from the 6 to 18 daily observations for which cloud cover was less than 30%. While uncertainties of individual vertical columns typically range from 50–105% (T. Kurosu, personal communication, 2008), the monthly mean at our resolution is the average of 150–350 data points, so that the standard error of the mean is small (3–5%). We found that the known distribu-

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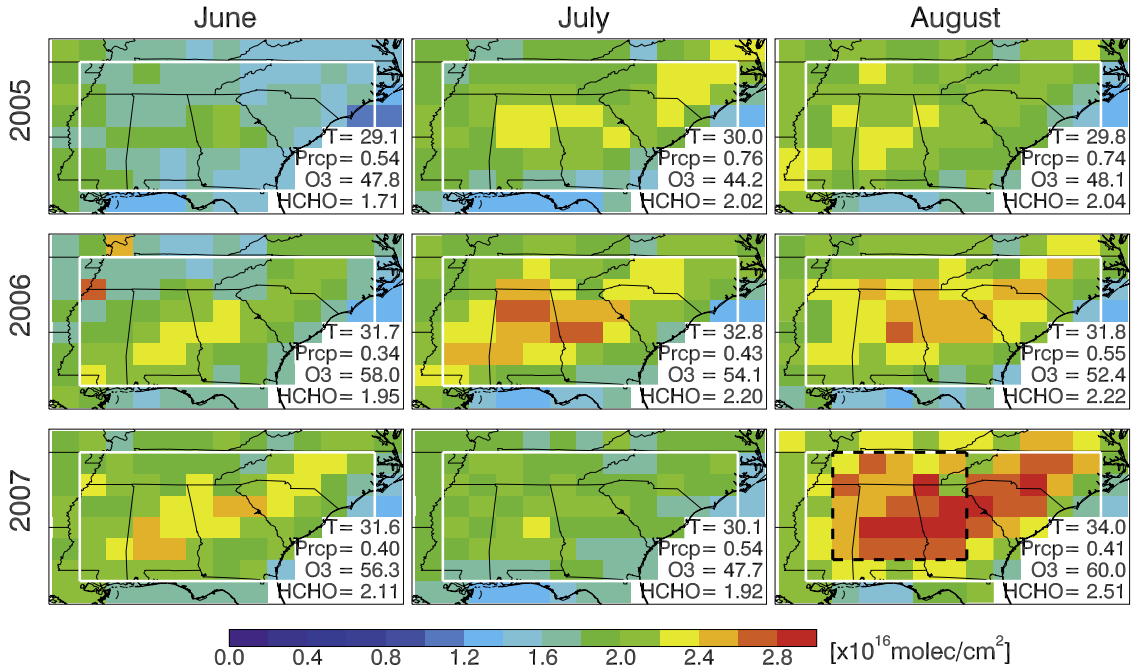

Figure 1. Monthly-average OMI HCHO column ($\times 10^{16}$ molec/cm^2) for the summers of 2005–2007. The numbers in the lower right hand corner of each panel are the average temperature at 2 m (T, °C) near the local overpass time, monthly-average total precipitation (Prcp, $\times 10^{-4}$ kg/m^2/s)), observed surface ozone (O3, ppbv), and formaldehyde column (HCHO, $\times 10^{16}$ molec/cm^2) of all gridboxes within the white box (Region A), excluding gridboxes containing only ocean. The area within the box outlined with black dashes (Region B) is the region most impacted by the 2007 drought (U.S. Drought Monitor, http://www.drought.unl.edu/dm/monitor.html).

tion of plants with various isoprene emission rates is discriminated in the OMI HCHO data; for the contiguous U.S. in summer, the monthly average OMI HCHO columns are well correlated (R^2 = 0.45–0.56, $p < 0.01$) with landscape-average isoprene emission factors from the Model of Emissions of Gases and Aerosols from Nature (MEGAN) [*Guenther et al.*, 2006].

[7] There are two potential factors to confound our analysis, though we argue that neither is significant for our purposes. First, forest fires and agricultural burning are direct sources of HCHO. However, we found that fires were not statistically significant sources of variability for our study period according to MODIS fire-counts. Second, a shape factor for the vertical distribution of HCHO within the column is assumed in the conversion of a slant to a vertical column [*Palmer et al.*, 2001]. For the vertical columns shown here, the monthly-average shape factors were taken from the GEOS-Chem chemistry and transport model for 2006 with transport driven by the GEOS-4 assimilation system [*Bloom et al.*, 2004]. Therefore, there is the potential that the vertical column may be biased by the shape factor. We believe this bias is unimportant as the daily vertical and slant columns are well correlated (e.g., $R^2 = 0.94$, $p < 0.01$ for June 2007 for viewing angles <45°).

3. Sources of Variability

[8] There are a number of factors that can cause variability in isoprene emissions. In this section, we assess the influence of temperature on isoprene emissions as inferred by variations in the OMI HCHO column. We discuss factors, both real and artificial, that complicate this analysis, making it a challenging task to separate the variation of inferred isoprene emissions associated with temperature from those of other temperature-dependent factors. All correlation coefficients presented in this section have a confidence level of 98% or 99%.

[9] Figure 1 shows the monthly-average HCHO columns for June, July and August over the southeastern U.S. from 2005–2007. The highest average column for Region A occurred in August 2007 (2.5×10^{16} molec/cm^2), which is about 50% higher than the lowest column in June 2005 (1.7×10^{16} molec/cm^2). The highest columns of the 1° latitude by 1.25° longitude gridboxes within Region A are about 100% greater than the lowest ones.

[10] The inferred variability of regional, monthly-average isoprene emissions from the HCHO columns is about 22% for the summers of 2005–2007. Our result agrees with the finding of *Palmer et al.* [2006], who estimated that the interannual variations in the GOME-derived isoprene emissions between 1996 and 2001 for June, July and August were 27, 22, and 35%, respectively, and *Abbot et al.* [2003] who estimated 30% variation for 1995–2001.

3.1. Temperature

[11] Figure 1 shows the monthly, regional-average surface temperature from the GEOS-5 fields near the overpass time of the Aura satellite and the monthly, regional-average precipitation for the southeastern U.S. Of the three, the summer of 2005 was the coolest and wettest, while the summers of 2006 and 2007 were comparatively warmer and drier. There was often significant spatial variability in

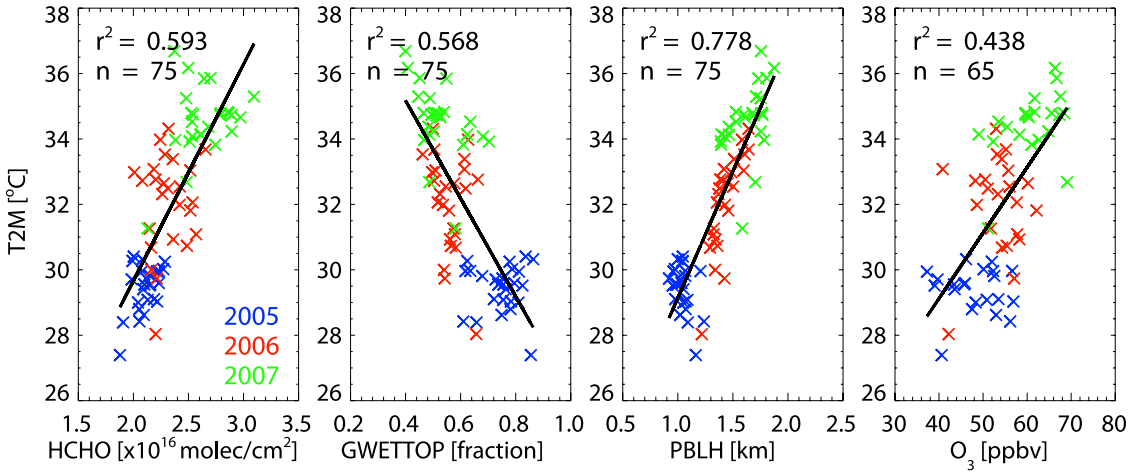

Figure 2. The August-average GEOS-5 afternoon surface temperature (T2M) versus OMI HCHO columns ($\times 10^{16}$ molec/cm^2), soil moisture (GWETTOP), and the afternoon mixed layer height (PBLH) for gridboxes in Region B. The monthly-average EPA surface ozone (2 pm) versus surface temperature is also shown for gridboxes with observations.

rainfall and temperature throughout the region. The regional-average temperature was lowest in June 2005 (29°C), coincident with the lowest average HCHO column, and highest in August 2007 (34°C), coincident with the highest average column. Figure 2 shows the August-average surface temperature versus HCHO columns. The columns are linearly and well correlated ($R^2 = 0.59$) with temperature for 25–37°C. This result supports that temperature is a major source of variability for isoprene emissions, as found in other studies using the GOME data [*Abbot et al.*, 2003; *Palmer et al.*, 2006].

3.2. Temperature-Dependent Variables

[12] As discussed in section 1, experimental evidence shows the strong dependence of isoprene emissions on temperature. In addition to temperature, variation of the HCHO column is possibly associated with at least three other variables that are temperature-dependent and, subsequently, non-independent.

[13] First, the OMI HCHO column is anti-correlated with both topsoil ($R^2 = 0.13–0.43$; Figure 3) and root zone ($R^2 = 0.11–0.42$) moisture in Region B; this region, as defined in Figure 1, was the epicenter of the historic 2007 drought. These correlations suggest that drought does cause variation in isoprene emissions, though the correlations are not themselves conclusive as the underlying cause of the correlation is likely that drought is convolved with temperature, a non-independent variable. There is a strong anti-correlation between topsoil moisture and surface temperature ($R^2 = 0.57$, Figure 2) and between root zone moisture and temperature ($R^2 = 0.48$). This result indicates that drought is associated with high temperature.

[14] Second, high surface ozone is associated with high temperatures [e.g., *Galbally*, 1971] and harms vegetation, stimulating isoprene production [*Fares et al.*, 2006]. Observed surface ozone from the Environmental Protection Agency Air Quality System varies linearly with the HCHO column ($R^2 = 0.53$) and with temperature ($R^2 = 0.44$, Figure 2). The production of ozone in the southeastern U.S. is typically limited by the availability of NO_x and not peroxy radicals generated during the oxidation of isoprene [*Chameides et al.*, 1988; *Fiore et al.*, 2005]. (In fact, high levels of isoprene can serve as a sink for NO_x through the formation of nitrates, but there is considerable uncertainty as to the amount of isoprene nitrates recycled back to NO_x [*Horowitz et al.*, 2007].) Therefore, the correlation of the HCHO column and surface ozone is mostly likely due to the temperature dependence of isoprene emissions and ozone formation, not because of the photochemical dependence of ozone formation on isoprene levels.

[15] Third, the mixed layer height is correlated with the HCHO column ($R^2 = 0.50$) and with temperature ($R^2 = 0.78$, Figure 2). The temperature dependence of the mixed layer height is an issue because the OMI's sensitivity to HCHO is altitude dependent. *Martin et al.* [2002] found for the GOME NO_2 that the calculated air mass factors, which are used to convert slant column measurements into total vertical columns, vary by about 15% per 100 hPa difference in the mixed layer height. That is, if the emission rate is held fixed, the chance that an individual molecule will be detected by the instrument increases with the mixed layer depth. The differences between the daily minimum and maximum GEOS-5 mixed layer depths are ~1 km, or ~100 hPa. Therefore, based on the estimate of *Martin et al.* [2002] and noting that shape factors for HCHO and NO_2 are similar as they are both driven by the mixed layer height, we expect this error to have the greatest effect, ~15%, between HCHO columns associated with the lowest and highest mixed layer heights. A better estimate of the magnitude of this error will account for variations with the trace gas profile, surface reflectivity, clouds, aerosols, etc.

4. Discussion and Conclusions

[16] Experimental data demonstrate that isoprene emissions are a strong function of temperature and the main driver of variability [e.g., *Tingey et al.*, 1979]. *Palmer et al.* [2006] showed that 75% of the monthly variation in the GOME-derived isoprene emissions over the southeastern U.S. is due to variations in temperature. However, part of

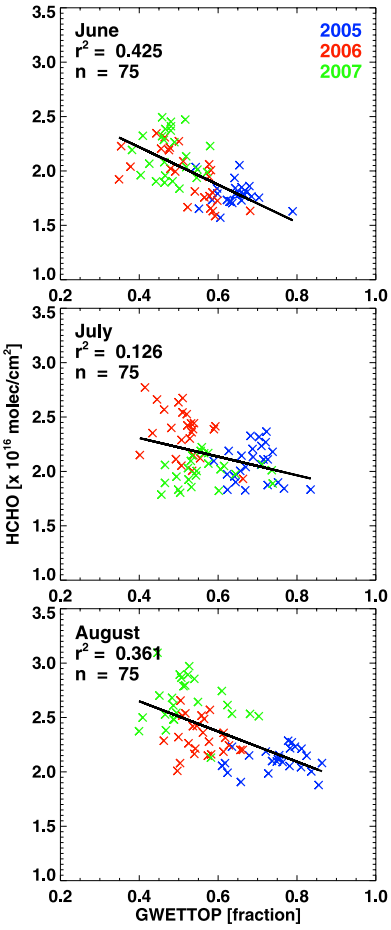

Figure 3. The monthly-average OMI HCHO columns ($\times 10^{16}$ molec/cm^2) versus GEOS-5 topsoil moisture for each gridbox in Region B.

the variation of the HCHO columns attributed to temperature may be related with other non-independent variables, such as drought, surface ozone and the detection sensitivity of the OMI with altitude.

[17] We found that the variation in the HCHO column is correlated with drought, but this does not prove causation as surface temperature and drought are well correlated in the southeastern U.S. [e.g., *Karl and Young*, 1987]. As discussed in section 1, experimental evidence shows that isoprene emissions from plants tend to change little during short-term drought. However, one would expect isoprene emissions to decrease during the historic drought in 2007 [*Luo and Wood*, 2007; *Mo and Schemm*, 2008] if it were severe enough that trees shed leaves prematurely and/or died. Cities in Region B received only about half to two-thirds of their normal precipitation in all of 2007, though rainfall occurred nearly every month, helping to maintain some soil moisture. In fact, much of Region B received half to near normal rainfall in July and August 2007. While the drought was historic and trees were certainly under stress, there was not an extended period without any rainfall. Consequently, the majority of trees may have responded to the drought as if it were "short-term" (i.e., with <20% variation of the isoprene emissions rate) as opposed to "long-term", which is consistent with the report that premature leaf shedding did not begin in Georgia until September [*Raines*, 2007].

[18] In the southeastern U.S., drought typically begins because of a lack of large-scale moisture influx, such as associated with a westward expansion of the Bermuda High. The combination of drought and high temperatures causes evapotranspiration to decrease, which deepens the drought through decreased precipitation recycling (i.e., the contribution of local evaporation to local precipitation), further increasing air temperature [e.g., *Dirmeyer*, 1994; *Trenberth*, 1999]. Therefore, through this positive feedback, drought can indirectly enhance isoprene emissions, particularly in Region B in August 2007, which was characterized by observed maximum temperatures higher than 37°C for more than 50% of the days.

[19] We performed a regression analysis of the HCHO column (dependent variable) with the "independent" variables, surface temperature and soil moisture, for the region hardest hit by the drought (i.e., Region B). The regression coefficient for soil moisture was actually positive, contrary to the relation shown in Figure 2. Consequently, our regression analysis likely did not give valid results about either of these two variables because their cross-correlation was high ($R^2 = 0.40$).

[20] In summary, the variation of isoprene emissions, as inferred from the OMI HCHO data, is predominantly caused by variation in temperature, which is in agreement with experimental evidence. However, part of the correlation of HCHO and temperature is associated with temperature-dependent variables, such as ozone and the detection sensitivity of the OMI, which we argue both enhance the HCHO column as temperature increases. In addition, the decrease in evapotranspiration during drought would act to increase temperature and, subsequently, to increase isoprene emissions. Therefore, it is a challenging, if not impossible, task to separate the impact of temperature from that of the individual impacts of temperature-dependent variables on isoprene emissions as inferred from HCHO column data over the southeastern U.S.

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